

USSR

UDC 547.26'118 + 543.226

PUDOVIK, A. N., KONOVALOVA, I. V., ANOSHINA, N. P., and ROMANOV, G. V.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy
of Sciences USSR and Kazan' State University imeni Ul'yanov-Lenin

"Determination of the Activation Energy of the Phosphonate-Phosphate
Rearrangement and of Some Other Reactions by the Method of Differential-
Thermal Analysis"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 10, Oct 73, pp 2153-2156

Abstract: Determination of the activation energy of the decomposition of sodium bicarbonate, isomerization of the ethylphosphonous acid diallyl ester, phosphonate-phosphate rearrangement, and the breakdown of α -hydroxyalkylphosphonates and their analogs was carried out by means of the differential thermal analysis (DTA). A satisfactory agreement has been achieved between the calculated and literature data. It has been shown that DTA may be used in determining E_{act} for thermal reactions of α -hydroxyalkylphosphonates.

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UDC 661.718.1

PUDOVIK, M. A., and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Synthesis of 2-Oxo-1,3,2-diazaphospholanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 10, Oct 73, pp 2147-2149

Abstract: To a solution of 0.05 g-mole of 2-chloro-1,3-dialkyl-1,3,2-diazaphospholane in 60 ml of anhydrous benzene a mixture of 0.05 g-mole water, 0.05 g-mole triethylamine, and 15 ml tetrahydrofuran was added at 10-20°. After 12 hrs at room temperature the base hydrochloride and the solvent were removed, the residue distilled in high vacuum yielding 2-oxo-1,3-dialkyl-1,3,2-diazaphospholanes -- colorless liquids. The NMR and IR spectral characteristics of these compounds have been investigated.

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USSR

UDC 661.718.1

PUDOVIK, M. A., and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Synthesis of 2-Cxo-3-phenyl-1,3,2-oxazaphospholanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 10, Oct 73, pp 2144-2147

Abstract: To a solution of 2-chloro-3-phenyl-1,3,2-oxazaphospholane in benzene a mixture of water, triethylamine and tetrahydrofuran is added dropwise. After 24 hrs storage and removal of triethylamine hydrochloride, a viscous mass is obtained which becomes crystalline; after recrystallization from benzene the 2-oxo-3-phenyl-1,3,2-oxazaphospholane (I) melts at 86-87°. Two other approaches via hydrolysis or acidolysis of 2-diethylamino-3-phenyl-1,3,2-oxazaphospholane failed to yield pure (I). Geometrical isomerism has been noted in a series of five membered phosphites containing a nitrogen atom in the ring, from the analysis of ¹H and ³¹P NMR data.

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UDC 547.26'118:541.49

KURAMSHIN, I. Ya., MURATOVA, A. A., YARKOVA, E. G., MUSINA, A. A., IZMAYLOVA, F. Kh., and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

"S-Alkyl Esters of the Thio- and Dithioacids of Phosphorus (IV) and Their Complexes With Tin"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 7, Jul 73, pp 1456-1466

Abstract: A series of thio- and dithioesters of thiophosphoric and thio- and dithiophosphinic acids was synthesized and characterized. Their IR and NMR spectra were studied. It was shown that the conformational isomerism in S-methyldialkylthio- and dithiophosphinates is caused by the P-C bond rotation. Complexes of S-alkylthiophosphates and thiophosphinates with tin tetra- and alkylhalides were obtained. Their IR and NMR spectra were studied. It was shown that in solutions the complexes $[R_2P(O)(SCH_3)]_2SnX_4$ exist as mixtures of geometrical isomers. It was shown that with coordination, a redistribution of the electronic density of the P-S bond takes place on account of the inductive and mesomeric effects. Both in the free state and as complexes the thioesters $R_2P(O)(SR')$ exhibit conformational isomerism. Based on the IR and NMR data, the electron donor ability of S-methyldialkyl-dithiophosphinates in relationship to tin halides was analyzed.

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UDC 547.26'118 + 547.446.1

PUDOVIK, A. N., GAZIZOV, T. Kh., and SUDAREV, Yu. I., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Reaction of Trimethylsilyl Diethyl Phosphite With Chloral"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 9, Sep 73, p 2086

Abstract: Trimethylsilyl diethyl phosphite reacts with chloral in ether solution at -60° yielding diethyl α -trimethylsiloxy- β,β,β -trichloroethylphosphonate (I), d_4^{20} 1.2474, n_D^{20} 1.4610. Heating (I) at $140-150^{\circ}/100$ mm for 16 hrs yields diethyl β,β -dichlorovinyl phosphate b.p. $127-128^{\circ}/12$ mm, d_4^{20} 1.2990, n_D^{20} 1.4490 and trimethylchlorosilane, b.p. $55-56^{\circ}$, d_4^{20} 0.8571, n_D^{20} 1.3855.

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UDC 547.26'118

PUDOVIK, A. N., ZIMIN, M. G., YEVDOKIMOVA, V. V., Kazan' State University
imeni V. I. Ul'yanov-Lenin

"Reaction of α - and β -Ketophosphonates With Compounds Containing Labile
Hydrogen Atoms"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 9, Sep 73, pp 1907-1910

Abstract: It was shown that dimethyl- and diethylphosphonoacetone is capable of condensing with cyanoacetic ester and dinitrile of malonic acid forming the diethyl ester of 2-methyl-3-cyano-3-carboethoxyallylphosphonic acid and the dialkyl ester of 2-methyl-3-cyano-3-carbamidoallylphosphonic acid. The reaction of chloral and benzaldehyde with the dibutyl esters of aceto- and benzoylphosphonic acids and N,N-tetraethyldiamidoacetophosphonic acid take place at the carbonyl groups of the latter, forming dibutyl α -trichloroacetoethyl(benzoylbenzyl)phosphates and N,N-tetraethylalkyldiamido-phosphates.

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UDC 547.26'118

PUDOVIK, A. N., ZIMIN, M. G., SOBANOV, A. A., and EVSTAF'YEV, G. I., Kazan'
State University imeni V. I. Ul'yanov-Lenin

"Reactions of α -Hydroxyallylphosphonic Esters"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 9, Sep 73, pp 1910-1915

Abstract: It was shown that the dimethyl ester of α -hydroxyallylphosphonic acid upon heating with catalytic amounts of alkoxides or trimethylamine are converted to the propionate of the dimethyl ester of α -hydroxyallylphosphonic acid. A route of the formation of the propionate was proposed including the initial isomerization of the α -hydroxyallylphosphonic ester into the ester of propionephosphonic acid followed by its reaction with a second molecule of α -hydroxyallylphosphonic ester. It was shown that the reaction of α -ketophosphonic acid esters with α -hydroxyalkylphosphonates takes place with the formation of dialkyl phosphites, esters of carboxylic acids, and dialkyl esters of α -dialkylphosphonalkylphosphonic acid. Heating the dialkylesters of α -hydroxyallylphosphonic acid in acetic acid or anhydride in presence of sulfuric acid leads to their acetylation.

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USSR

UDC 547.241

PUDOVIK, A. N., GAREYEV, R. D., and SHTIL'MAN, S. Ye., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Enolization of the Ethyl Ester of α -Dimethoxyphosphinylacetoacetic Acid"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 7, Jul 73, pp 1646-1647

Abstract: The adduct of the "aldol" type reaction of ethyl diazoacetate with dimethoxyacetophosphonate breaks down in refluxing dioxane, yielding nitrogen and the ethyl ester of α -dimethoxyphosphinylacetoacetic acid. In this compound the ratio of the tautomeric forms was the following: cis-enol form: trans enol form: ketone form = 69.1:21.4:9.5,

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USSR

UDC 547.313.2:547.341

PUDOVIK, A. N., and YASTREBOVA, G. Ye., Kazan' State University

"Reaction of Trialkylphosphites With α -Bromovinylphosphonates"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 7, Jul 73, pp 1647-1648

Abstract: Heating the diethyl ester of α -bromovinylphosphonic acid with a small excess of trimethyl- or triethyl phosphite yields 1-dimethoxyphosphone-2-diethoxyphosphone-ethylene, and 1,2-diethoxyphosphone-ethylene.

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UDC 747.341.139.31 + 547.391

PUDOVIK, A. N., BATYYEVA, E. S., IL'YASOV, A. V., NESTERENKO, V. D.,
MUKHTAROV, A. Sh., and ANOSHINA, N. P.

"Reactions of Trivalent Phosphorus Acid Amides With p-Quinones"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 7, Jul 73, pp 1451-1456

Abstract: Reaction of N-acetamides of dialkylphosphorous acids with p-quinones has been studied. Analogously to N-arylamidophosphites the N-acetamidophosphites react easily with p-benzoquinone, chloranil, and α -naphthoquinone forming crystalline addition products -- O,O-dialkyl O-p-hydroxyaryl N-acetimidophosphates. Using the EPR method, the possibility of a single electron transfer in the reactions of trivalent phosphorus acid amides with p-quinones was demonstrated going through an intermediate ion-radical formation.

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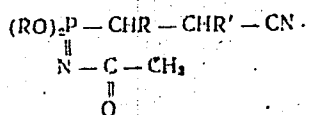
UDC 547.341.26'.118.07

PUDOVIK, A. N., BATYYEVA, E. S., NESTERENKO, V. D., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov

"A Method of Producing 0,0-Dialkyl-N-Acetimido- β -Cyanalkylphosphonates"

Moscow, Otkrytiya, Izobreteniya, Promyshlennyye Obrazttsy, Tovarnyye Znaki, No 16, Jun 73, Author's Certificate No 375299, Division C, filed 27 Aug 71, published 23 Mar 73, pp 51-52

Translation: This Author's Certificate introduces: 1. A method of making 0,0-dialkyl-N-acetimido- β -cyanalkylphosphonates of the general formula



where R and R' are hydrogen or an alkyl. As a distinguishing feature of the patent, an 0,0-dialkyl-N-acetamidophosphite is reacted with a nitrile of an α,β -unsaturated carboxylic acid with subsequent isolation of the goal product by conventional methods. 2. A modification of this method distinguished by the fact that the process is carried out in an organic

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PUDOVIK, A. N., et al., Otkrytiya, Izobreteniya, Promyshlennyye Obrazttsy, Tovarnyye Znaki, No 16, Jun 73, Author's Certificate No 375299, Division C, filed 27 Aug 71, published 23 Mar 73, pp 51-52

solvent such as benzene with the application of heat. 3. A modification of the method covered in point 1 distinguished by the fact that the process is done in the presence of an alkali metal alcoholate such as sodium ethylate as a catalyst.

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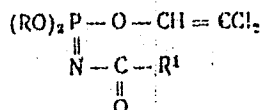
UDC 547.261.118.07

PUDOVIK, A. N., BATYYEVKA, Ye. S., and NESTERENKO, V. D., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov

"A Method of Synthesizing O,O-Dialkyl-O-Dichlorovinyl-N-Acylimidophosphates"

Moscow, Otkrytiya, Izobreteniya, Promyshlennyye Obraztsy, Tovarnyye Znaki, No 16, Jun 73, Author's Certificate No 375297, Division C, filed 27 Sep 71, published 23 Mar 73, p 51

Translation: This Author's Certificate introduces a method of synthesizing O,O-dialkyl-O-dichlorovinyl-N-acylimidophosphates of the general formula



where R and R¹ are an alkyl. As a distinguishing feature of the patent, an O,O-dialkyl-N-acylamidophosphite is reacted with chloral in an organic solvent such as benzene in the presence of a hydrogen chloride acceptor such as trimethylamine with subsequent isolation of the goal product by conventional methods.

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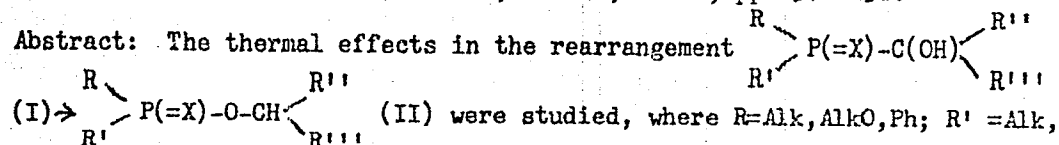
UDC 547.26'118+543.226

ROMANOV, G. V., YAGFAROV, M. Sh., KONOVALOV, A. I., FUDOVIK, A. N., KONOVALOVA, I. V., and YUSUPOVA, T. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR, and Kazan' State University imeni V. I. Ul'yanov-Lenin, Kazan'

"The Thermodynamic and Kinetic Characteristics of the Phosphonate-Phosphate Rearrangement"

Leningrad, Zhurnal Obshchey Khimii, Vol 43, No 11, pp 2378-2386

Abstract: The thermal effects in the rearrangement



AlkO, Ph, OH; R'' = H, Me, Ph, COOAlk; R''' = COOAlk, COMe, P(O)(OR)₂, CN; X = O, S. The heat capacities at -50 - +120° and the changes in enthalpy during the rearrangement I → II at the temperature of the reaction were determined for a number of compounds I. It was shown that an approximately linear relation exists between the temperatures at which the reaction begins and the logarithms of the velocity constants of the isomerization of compounds I determined at a single temperature.

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USSR

UDC 547.26'118:541.49

MURATOVA, A. A., YARKOVA, E. G., PLEKHOV, V. P., SAFIULLINA, N. R., MUSINA, A. A., and PUDOVNIK, A. N., Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Stereoisomers of Partial Esters of Phenylphosphonous Acid and Their Complexes With Stannic Chloride"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 8, Aug 73, pp 1692-1696

Abstract: Complexes of partial esters of phenylphosphonous acid with stannic chloride were synthesized yielding $[(RO)C_6H_5P(O)H]_2 \cdot SnCl_4$ where R - methyl, ethyl, n-propyl, iso-propyl, and n-butyl. A detailed analysis of IR- and PMR- spectral data was carried out. It was proposed that the stereoisomerism of these complexes is due to different orientation of the phenyl ring plane in the phenylphosphonite with respect to the P-H bond.

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UDC 547.241:541.49

USSR

PUDOVIK, A. N., MURATOVA, A. A., KURAMSHIN, I. Ya., YARKOVA, E. G., and
VINOGRADOV, L. I., Kazan State University imeni V. I. Ul'yanova - Lenina

"Reaction of α -Methylmethylphosphones of Dialkylphosphinic and Dialkylthio-
phosphonic Acids With Stannic Chloride and Stannic Bromide"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 5, 1972, pp 979-986

Abstract: The title reaction -- for alkyl = methyl, butyl, cyclohexyl, and phenyl -- proceeds in methylene chloride forming complexes of the general form $[R, R'P(O)OH]_2SnX_4$ or $[RR'P(O)SH]_2SnX_4$ for equimolar mixtures of the two starting compounds. IR studies of the products of a starting mixture having a 2:1 ratio of reactants indicate that dimerization has occurred. When the reaction occurs with the elimination of the halogen acids, the salt $[RR'P(O)]_2SnX_2$ is formed which indicates an intramolecular rearrangement resulting in a polymer. A number of conclusions about the nature of these complexes were drawn from detailed NMR and IR studies.

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USSR

UDC 547.341.791

PUDOVIK, A. N., KHUSAINOVA, N. G., and NASYBULLINA, Z. A., Kazan' State University

"Cycloaddition of Phenylazide to Propynylphosphonates and Propynylphosphine Oxides"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 8, Aug 73, pp 1683-1686

Abstract: Cycloadditions of phenylazide to 0,0-dipropyl propynylphosphonate, diphenylpropynylphosphine oxide, diethylpropynylphosphine oxide and propynylphosphonic acid chloride occur smoothly in 20-30 hrs when heated to 105-110° in anhydrous toluene. The products are 4-phosphinyltriazoles-1,2,3 obtained in 47-60% yield.

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USSR

UDC 547.341.139.81 + 547.391

PUDOVIK, A. N., BATYYEVA, E. S., and GIRFANOVA, Yu. N.

"Reactions of Trivalent Phosphorus Acid Amides With Maleinimides"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 8, Aug 73, pp 1696-1701

Abstract: Anilides of dialkylphosphorous acids react with maleinimides forming phosphoric ylides, i.e., the amide group proton is less labile than the proton of the heteroring, so that the stabilization of the intermediate bipolar ion occurs through the participation of this proton. N-Phenyl, N-acetyl and N,N-dialkylamides of dialkylphosphorous acids react with substituted and unsubstituted maleinimides forming respective succinimidyldiene-0,0-dialkyl-N-amidophosphoranes. It was shown that the hydrolysis of N-arylsuccinimidyldiene-0,0-dialkyl-N-arylamidophosphoranes leads to the formation of N-aryl-4-0,0-dialkylphosphonesuccinimide.

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USSR

UDC 547.341

PUDOVIK, A. N., GAREYEV, R. D., STABROVSKAYA, L. A., YEVSTAF'YEV, G. I., and REMIZOV, A. B., Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Reactivity of Unsaturated Organophosphorus Compounds in the Reaction of 1,3-Dipolar Cycloaddition of Diaryldiazomethanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 8, Aug 73, pp 1674-1682

Abstract: The kinetics of the 1,3-dipolar cycloaddition reaction of diaryldiazomethanes with organophosphorus dipolarophiles at 60° in m-xylene was investigated. The reaction mechanism is based on a single stage polycentric process with a cyclic electron transfer. The established order of dipolarophilic activity of the unsaturated organophosphorus compounds agrees well with current concepts of the effect of substituents at the phosphorus atom: additive manifestation of the inductive effect and the ability of the substituents to conjugate with the main system.

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USSR

UDC 661.718.1 + 547.879

PUDOVIK, M. A., TERENT'YEVA, S. A., and PUDOVIK, A. N., Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Acad. Sc. USSR

"Reaction of 2-Alkoxy-4,5-benzo-1,3,2-oxazaphospholanes With Hexaalkyl-triaminophosphines"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Aug 73, p 1860

Abstract: Heating 2-alkoxy-4,5-benzo-1,3,2-oxazaphospholanes with hexaalkyltriaminophosphines at 120-140° leads to the formation of oxazaphospholanes with a geminal system P-N-P. A mixture of 10 g of 2-methoxy-4,5-benzo-1,3,2-oxazaphospholane and 9.7 g hexamethyltriaminophosphine was heated to 110-130° for 1 hr yielding 47% of 2-methoxy-3-bis(dimethylamino)-phosphino-4,5-benzo-1,3,2-oxazaphospholane, b.p. 111°/0.007 mm, d_4^{20} 1.1577, n_D^{20} 1.5610. In a similar fashion, starting from 2-isopropoxy-4,5-benzo-1,3,2-oxazaphospholane and hexaethyltriaminophosphine, 2-isopropoxy-3-bis-(diethylamino)phosphino-4,5-benzo-1,3,2-oxazaphospholane was obtained, b.p. 130°/0.025 mm, d_4^{20} 1.0744, n_D^{20} 1.5338.

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UDC 541.124

PUDOVIK, A. N., CHERKASOV, R. A., SUDAKOVA, T. M., and YEVSTAF'YEV, G. I.,
Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Addition of Phosphorus Dithioacids to the C≡N Bond"

Moscow, Doklady Akademii Nauk SSSR, Vol 211, No 1, Jul-Aug 73, pp 113-115

Abstract: The reactions of diisopropyldithiophosphoric acid with benzonitrile and the reaction of diphenyldithiophosphinic acid with benzonitrile, cyanoacetic ester and diethyl cyanomethylphosphonate were investigated. Diisopropyldithiophosphoric acid adds to benzonitrile in an equimolar ratio, in the cold, and without any catalysts. Thiobenzamide precipitates after 10-12 days. Treating this mixture with pentane, followed by separation of solid thiobenzamide and cooling the pentane to -10° yields yellow crystalline O,O-diisopropyl S-benzylimidoaldithiophosphonate m.p. $58-59^{\circ}$. Diphenyldithiophosphinic acid reacts easily with benzonitrile at room temperature yielding thiobenzamide and tetraphenyltrithiopyrophosphate regardless of the ratio of reagents taken. Analogous reaction course is observed in case of the other reagents mentioned. Thus it has been shown that phosphoric dithioacids add to the C≡N bond forming imidoaldithiophosphates -- expressed thiophosphorylating agents.

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Organophosphorus Compounds

USSR

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PUDOVIK, A. N., KURAMSHIN, I. YA., YARKOVA, E. G., MURATOVA, A. A., MUSINA, A. A., and MANAPOV, R. A., Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Study of the Reaction of Methyl Ester and Acid Chloride of Dimethylphosphinic Acid and Their Thione Analogues With Tin Halides"

Leningrad, Zhurnal Obshchey Khimii, Vol 43(105), No 6, Jun 73, pp 1229-1236

Abstract: Complexes of O-methyldimethylphosphinate and acid chloride of dimethylphosphinic acid with tin tetra- and alkyl halides have been obtained and characterized. Their IR, NMR, and NGR spectra have been studied, establishing that the coordination is due to the donor properties of the phosphoryl group oxygen. It has been shown that $\Delta \nu (\text{P=O}) / \nu_{\text{O}} (\text{P=O})$ of the O-methyldimethylphosphinate and acid chloride of the dimethylphosphinic acid changes symbatically with $\sum \sigma^*$ of the substituents at the tin atom. A linear relationship has been established for the stannic chloride complexes with dimethylphosphinic acid between $\Delta \nu (\text{P=O}) / \nu_{\text{O}} (\text{P=O})$ and $\sum \sigma_{\text{P}}$ of the substituents at the phosphorus atom. It has been shown that the thiophosphoryl sulfur has a lower donor ability than the phosphoryl oxygen. Geometrical structure of the obtained complexes has been discussed.

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USSR

UDC 547.341

PUDOVIK, A. N., GAREYEV, R. P., STABROVSKAYA, L. A., and AGANOV, A. V.,
Kazan' State University Imeni V. I. Ul'yanov-Lenin

"1,3-Dipolar Cycloaddition of 9-Diazofluorene to Unsaturated Organic Phosphorus Compounds"

Leningrad, Zhurnal Obshchey Khimii, Vol 43, (105), No 6, Jun 73, pp 1236-1240

Abstract: The reactions of 9-diazofluorene with unsaturated organic phosphorus compounds at room temperature pass through the formation of intermediate products -- Δ^1 -pyrazolenes, which, depending on experimental conditions, break down to nitrogen and cyclopropene derivatives, or isomerize to Δ^2 -pyrazolenes. In comparison to diphenyldiazomethane, 9-diazofluorene is less reactive in regard to its enophilic activity in the reactions of 1,3-dipolar cycloaddition to organic phosphorus dipolarophiles. When 9-diazofluorene was reacted with dimethoxyvinylphosphonate at about 80°C, the product was 1-dimethoxyvinyl-2-biphenylenecyclopropane.

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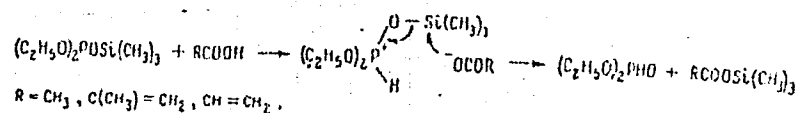
UDC 547.26'118

GAZIZOV, T. KH., KHARLANOV, V. A., and PUDOVNIK, A. N., The Institute of Organic and Physical Chemistry imeni A. Ye. Arbutova, Academy of Sciences USSR

"The Reaction of Trimethylsilyl Diethyl Esters of Phosphorous Acid with Organic Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 11, 1972, pp 1579-1580

Abstract: The title reaction using acetic acid proceeds with the formation of diethylphosphorus acid and trimethylsilyl acetate according to the following reaction:



The analogous reaction occurs with methacrylic and acrylic acids. Thus, these substituted phosphorous acids react with either saturated or with α, β -unsaturated organic acids by the Arbuzov reaction due to the initial protonation of the phosphorous atom of the silophosphorous acid.

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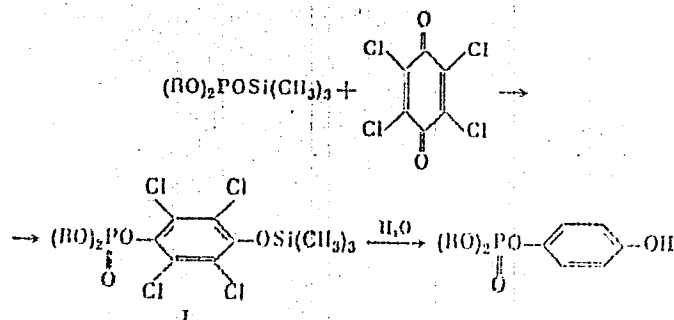
UDC 547.241+547.391

PUDOVIK, A. N., BATYYEVA, E. S., and ZAMALETDINOVA, G. U.

"The reaction of Trimethylsilyl Diethyl Phosphite with Chloranil"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 11, 1972, p 2577

Abstract: The title reaction was carried out with heating in anhydrous ether under an atmosphere of argon with the formation of crystalline diethyl p-trimethylsilyloxytetrachlorophenyl phosphate as follows:



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PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 42(104), Vyp 11, 1972, p 2577

The structure was confirmed by NMR of P^{31} and the hydrolysis reaction. The chemical shift from NMR was characteristic of the phosphate structure. Paramagnetic resonance spectra also indicated a signal from the protons of the Me_3 .

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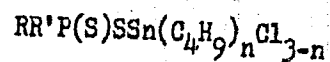
UDC 547.26*118:541.49

PUDOVIK, A. N., MURATOVA, A. A., KURAMSHIN, I. YA., and YARKOVA, E. G.,
Kazan State University imeni V. P. Ul'yanova-Lenina

"The Interaction of O,O-dimethyl Methylphosphonates With Ten Salts of the
Dithiol Acids of Phosphorous"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 11, 1972, pp 2408-2412

Abstract: A study was made of the acceptor characteristics of ten salts of
the title compounds having the general formula

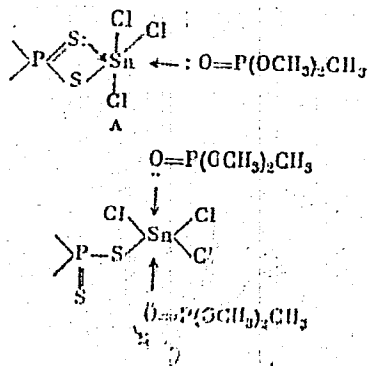


Where $R = R' = CH_3O, C_2H_5O$; $R = CH_3, R' = CH_3O$; for $n = 0, 1$, or 2
and $R_2P(S)S_2SnCl_2$ for $R = C_2H_5$ and $C_3H_7, (C_4H_9)_nS_2Cl_{4-n}$. The former can
accept one pair of electrons and will therefore form a 1:1 complex with the
phosphorus ethers; the latter two will accept 2 pairs and therefore form
1:2 complexes with these ethers. The electron donors were dimethyl ethers of
methylphosphonic acids. Ratios of 1:1 and 1:2 of the above reagents were
used for the following reaction:

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USSR

PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 42(104), Vyp 11, 1972, pp 2408-2412



A comparison of the spectra indicates the 1:1 complexes have a weaker tendency to dissociate than the 1:2 complexes. Preparation and physical data for the above compounds are given.

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USSR

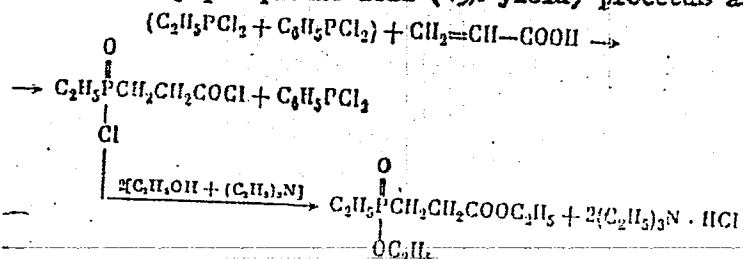
UDC 547.241.547.391.1

GASIZOV, T. KH., PASHINKIN, A. P., DMITRIYEVA, G. V., TUZOVA, L. L.,
KHAYRULLIN, V. K., and PUDOVIK, A. N., Institute of Organic and Physical
Chemistry imeni A. Ye. Arbutova, Academy of Sciences USSR

"Reactions of the Acyl Culonides of Trivalent-Phosphorus Acids with α, β -Unsaturated Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 8, 1972, pp 1730-1733

Abstract: A detailed study was made of the mechanism of the title reactions with special reference to behavior of the P atom of the chlorophosphines. The simultaneous reaction of the acrylic acid with equimolar mixtures of phenyl- and ethyldichlorophosphine (PDP and EDP, respectively) and the subsequent reaction with ethanol and triethylamine to form the ethyl ester of ethyl- β -carboethoxyethylphosphonic acid (45% yield) proceeds as follows:



USSR

GAZIZOV, T. KH., et al., Zhurnal Obshchey Khimii, Vol 42(104), Vyp 8, 1972, pp 1730-1733

An analagous reaction occurs between PDP and ethyldichlorophosphite. On the other hand, EDP, when treated with a mixture of acrylic and metacrylic acids reacts only with the former which is a strong electrophil. These two observations support the assumption that the P atom has a nucleophilic character. Thermal analysis and NMR data on P^{31} were used to elucidate the nature of the intermediates. IR spectra were also discussed.

2/2

USSR

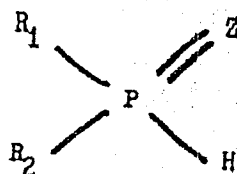
UDC 538.18-547.26*118.541.12

VINOGRADOV, L. I., ZIMIN, M. G., SAMITOV, YU. YU., and PUDOVIK, A. H.,
Kazan State University

"Spin-Spin Interaction of P^{31} Nuclei Directly Bonded to H^1 in Unsaturated
Esters of Phosphoric Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), No 8, 1972, pp 1724-1727

Abstract: The value of the spin-spin coupling constant $^1J_{PH}$ is most influenced
by the amount of S-character of the P-H bond. This parameter was measured
for 12 compounds having the general formula



for $Z=O$ and S and R_1 and R_2 being various alkyl, alkoxy, or halide-substituted
alkyl groups. It was correlated with the orbital symmetries and had values
ranging from 734 to 431 hertz. $^1J_{PH}$ is directly proportional to the square
 $1/2$

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USSR

VINOGRADOV, L. I., et al., Zhurnal Obshchey Khimii, Vol 42(104), No 8, 1972, pp 1724-1727

of the order of the bond P_{Sh}^2 and to the cube of the effective nuclear charge Z_{eff}^3 and thus can be written as:

$$\frac{\Delta^1 J_{PH}}{J_{PH}} \quad 2 \quad \frac{\Delta^P P_{Sh}}{P_{Sh}} \quad 3 \quad \frac{\Delta^Z Z_{eff}}{Z_{eff}}$$

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USSR

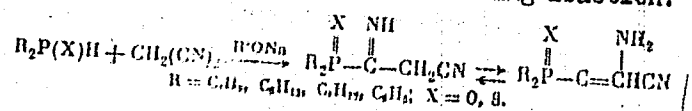
UDC 547.26'118

PUDOVIK, A. N., SUDAKOVA, T. M., RAYEVSKAYA, O. YE., and GEDECHKINA, V. A.,
Kazan State University imeni V. I. Ul'yanova-Lenina

"Reactions of Phosphonous Acids with the Malononitrile"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), No 8, 1972, pp 1727-1730

Abstract: On the basis of the rather large reactivity of the dialkyl- and diarylphosphonous acids, a study was made of the addition of diphenyl, dibutyl-, dihexyl-, and dioctylphosphonic acids to malononitrile. Heating a mixture of the phosphonic acids with malononitrile in benzene or hexane to 80°C for 2-3 hours resulted in the following reaction:



Both a 1:1 mixture of the reagents and a mixture containing an excess of the phosphonous acid resulted in a product containing 1 atom of each reactant. IR spectra indicate that the simple addition product undergoes imino-amino tautomerization, as in the above equation, and also intermolecular hydrogen

1/1

USSR

UDC 547.438.1+547.26*118+543.226

PUDOVIK, A. N., KONOVALOVA, I. V., ROMANOV, G. V., FIRSEVA, R. G., and
BURMISTROVA, N. P.

"Study of Phosphonate-phosphate Regrouping and the Processes accompanying It
by the Differential Thermal Analysis Method with Simultaneous Recording of
the Electrical Conductivity"

Leningrad, Zhurnal Obshchey Khimii, Vol XLIII (CV), No 1, 1973, pp 41-45

Abstract: The study of phosphonate-phosphate regrouping and the processes
accompanying it by the thermographic method with simultaneous recording of
the electrical conductivity is continued. The thermal behavior of a series
of α -oxyalkyl phosphonates and substituted α -oxyethylphenyl phosphonic
acids was studied. The thermal conversion of α -oxyalkylphosphonates and
their analogs was preceded by ionization of the hydroxyl group on the α -carbon
atom. The study was made of the mechanism of thermal phosphonate-phosphate
regrouping.

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USSR

UDC 547.341:139.81+547.391

PUDOVIK, A. N., BATYEVA, E. S., NESTERENKO, V. D., and ANOSHINA, N. P.

"Reaction of Analides of Dialkyl Phosphorous and Diaryl Phosphonous Acids with β -Quinones"

Leningrad, Zhurnal Obshchey Khimii, Vol XLIII (CV), No 1, 1973, pp 32-37

Abstract: In continuation of the study of the reactions of acid amides of trivalent phosphorous with compounds containing an activated carbonyl group [A. N. Pudovik, et al., Izv. AN SSSR, Ser. Khim., 510, 1972], a study was made of the reactions of analides of dialkyl phosphorous and diaryl phosphonous acids with different substituted and unsubstituted β -quinones and β -naphthoquinone. The amides of dialkylphosphorous and diaryl phosphonous acids react with β -quinones with the formation of O,O-dialkyl-O- β -hydroxy aryl- β -arylimido phosphates and phosphinates. The O,O-dialkyl-O- β -hydroxyaryl-N-arylimido phosphates are subjected to thermal regrouping into O-alkyl-O- β -alkoxyaryl-N-arylamido phosphates.

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USSR

(1)
UDC 547.26'118 + 547.442.2

GAZIZOV, T. Kh., KIBARDIN, A. M., PASHINKIN, A. P., SUDAREV, Yu. I., and
PUDOVIK, A. N., Institute of Organic and Physical Chemistry Imeni A. Ye.
Alduzov, Academy of Sciences, USSR

"Reactions of the Trimethylsilyldiethyl Ester of Phosphorous Acid With
Diacetyl"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, pp 679-680

Abstract: Reacting trimethylsilyldiethyl ester of phosphorous acid with
diacetyl at a temperature below 20° yields diethyl- α -trimethylsiloxy- α -
acetoethylphosphonate, b.p. 84-86°/1 mm, d_{20}^{20} 1.1180, n_D^{20} 1.4335. The
structure was confirmed by an independent synthesis from diethyl- α -
hydroxy- α -acetoethylphosphonate and trimethylchlorosilane and by IR and
NMR^{31P} spectroscopic analysis.

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USSR

UDC 547.26'118

FUDOVIK, A. N., FUDOVIK, M. A., and IVANOVA, L. K., Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Acad. Sc. USSR

"Reactions of 1,3,2-Diazaphospholanes With Acyl Halides"

Leningrad, Zhurnal Obshchey Khimii, Vol 42 (104), No 9, Sep 72, pp 1906-1910

Abstract: A series of 2-substituted N,N-di-tert-butyl-1,3,2-diazaphospholanes was synthesized. It was shown that, depending on the substituent at the phosphorus atom of diazaphospholanes, the reactions with acyl halides may occur with retention or breaking of the ring, forming derivatives of 3- or 4-coordinated phosphorus atom. With an exocyclic dialkylamino group the principal reaction is the exchange reaction with retention of the ring. Introduction of an alkoxy group makes the phosphorus atom a nucleophilic center, and the reaction goes via the Arbuzov rearrangement. In case of the 2-phenoxy derivatives of diazaphospholanes the reactions occur via one of the cyclic nitrogen atoms breaking the ring and forming derivatives of 3-coordinated phosphorus atom.

1/1

USSR

UDC 547.26'118:541.49

PUDOVIK, A. N., MURATOVA, A. A., and MEDVEDEVA, M. D., Kazan' State University
Imeni V. I. Ul'yanov-Lenin

"Reaction of n-Butyl Ester of Diethylphosphinous Acid With Triethyl Chlorostannate"

Leningrad, Zhurnal Obshchey Khimii, Vol 42 (104), No 9, Sep 72, pp 1910-1913

Abstract: The reaction of n-butyl diethylphosphinite with triethyl chlorostannate was investigated in detail. On the basis of differential-thermal analysis it has been shown that the reaction begins at 150-160° and is completed at 200-250°. Analysis of reaction products indicated that the reaction may go in two parallel directions: isomerization of the phosphinite with formation of a complex and an oxidation-reduction reaction between the donor and acceptor yielding several products. The later reaction is favored with increasing radicals of the phosphinite-alkoxy group and with transition from iodo- to bromo- to chloro-derivatives of tin.

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USSR

UDC 547.26'118

PUDOVIK, A. N., PUDOVIK, M. A., TERENT'YEVA, S. A., and GOL'DFARB, E. I.,
Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Acad. Sc.
USSR

"Reactions of the Derivatives of Trivalent Phosphorus With Orthoaminophenol"

Leningrad, Zhurnal Obshchey Khimii, Vol 42 (104), No 9, Sep 72, pp 1901-1906

Abstract: A mixture of isopropylphosphorous acid tetraethyldiamide and o-aminophenol was heated for 1-2 hrs at 130-140° to yield 2-isopropoxy-4,5-benzo-1,3,2-oxaazaphospholane (I), b.p. 95-97°/0.03 mm, m.p. 58-60°, and 1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5-phosphaspiro[4,4]nonane, m.p. 161-162°. 2-Ethoxy-4,5-benzo-1,3,2-oxaazaphospholane, b.p. 77-78°/0.03 mm, d_4^{20} 1.1948, n_D^{20} 1.5553 was obtained in an analogous manner. Sulfur added to molten (I) followed by heating for one hour at 100° gave 2-isopropoxy-2-thia-4,5-benzo-1,3,2-oxaazaphospholane b.p. 120-130°/0.03 mm, m.p. 92-94°. It has been shown that 2-ethyl-4,5-benzo-1,3,2-oxaazaphospholane undergoes protropic isomerization on storage, converting to 2-ethyl-4,5-benzo-1,3,2-oxaazaphospholene-2.

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USSR

UDC 541.6+541.49

FUDOVIK, A. N., KURAMSHIN, I. YA., MURATOVA, A. A., MANAPOV, R. A., YARKOVA, E. G., and MIFSAITOVA, G. M., Kazan' State University Imeni V. I. Ul'yanov-Lenin

"S-Alkyl Diethylthiophosphinites and Their Complexes with Stannic Chloride"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 5, May 73, p 1196

Abstract: IR spectra were studied of S-ethyl diethylthiophosphinite (I), S-n-propyl diethylphosphinite (II), diethylchlorophosphine (III), diethyl sulfide (IV) and tributylphosphine (V) in liquid state using solvents with different polarity. Analysis of the data on (I) and (II) indicated that these compounds exist as mixtures of two conformers arising from the rotation around the P-C bond, even though the rotation around the S-C bond could not be excluded. Following complexes were synthesized and studied: $[(C_2H_5)_2PR]_2SnCl_4$ where $R=C_2H_5S$, $n-C_3H_7S$, $[(C_2H_5)_2S]_2SnCl_4$ and $[(C_4H_9)_3P]_2SnCl_4$. These complexes were formed because of the donor properties of the phosphorus atom.

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USSR

UDC 547.26'118:541.49 /

MURATOVA, A. A., YARKOVA, E. G., PLEKHOV, V. P., ZAGETOVA, R. G., and
PUDOVIK, A. N.

"Study of Complexes of Dialkylphosphinous Acids With Tin, Titanium, and
Zirconium Halides"

Abstract: The authors studied reactions of di-n-butylphosphinous, diphenylphosphinous, dicyclohexylphosphinous, di-n-hexylphosphinous, di-n-octylphosphinous acids with tetrachlorides of tin, titanium, and zirconium and with tin tetrabromide. The obtained complexes had an $[R_2P(O)H]_2 \cdot MeX_4$ composition. Their infrared spectra were studied in the 400-4000 cm^{-1} region. The results are shown in a table containing information on 21 complexes.

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USSR

UDC 547.241 + 547.391

PUDOVIK, A. N., BATYYEVA, E. S., and ZAMALETDINOVA, G. U.

"Reaction of Trimethylsilylphosphite With 5-Benzalbarbituric Acid"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 4, Apr 73, p 947

Abstract: Reacting trimethylsilyldiethylphosphite with 5-benzalbarbituric acid and 1,3-diphenyl-5-benzalbarbituric acid in ether and under argon atmosphere yields 0,0-diethylbarbiturylbenzylphosphonate, m.p. 159-160° and 0,0-diethyl-1,3-diphenyl-barbituryl-5-benzylphosphonate, m.p. 133-134° respectively.

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USSR

UDC 547.26'118

PUDOVIK, A. N., KONOVALOVA, I. V., KAKURINA, V. P., and BURNAYEVA, L. A.,
Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Reactions of Monoisocyanates of Alkyleneglycolphosphorous Acids With the
Esters of α -Ketocarboxylic Acids and Phenylglyoxal"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, pp 553-556

Abstract: Isocyanates of ethylene- and 1,3-butyleneglycolphosphorous acids form 1:1 addition products with esters of pyroracemic, benzoylformic, α,β -diketobutyric acids and phenylglyoxal. On the basis of spectral data and sharp melting points bicyclic structures were assigned to these compounds. The reactions were carried out at -5 to 0° in methylene chloride, adding the carbonyl compounds dropwise to the isocyanate; the products crystallized on overnight standing. Esters of pyroracemic and benzoylformic acids form crystalline products with ethyleneglyoxalphosphorous acids, phenylglyoxal yields a dense liquid and the ester of α,β -diketobutyric acid — a glassy material.

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USSR

UDC 547.245'241

PUDOVIK, A. N., ROMANOV, G. V., NAZMUTDINOV, R. Ya., and KONOVALOVA, I. V.,
Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Academy
of Sciences, USSR, and Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Reaction of bis(Trimethylsilyl)hypophosphite With Methyl Pyrrolacetate"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, p 678

Abstract: Title reaction carried out in an atmosphere of argon at -5 to 0°
followed by overnight stirring at room temperature gave trimethylsilyl(α -
carboxomethoxy)ethylphosphite, b.p. $83^{\circ}/0.2$ mm, d_4^{20} 1.0857, n_D^{20} 1.4276.

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UDC 547.241 + 547.391

USSR

PUDOVIK, A. N., BATYYEVA, E. S., and ZAMALETDINOVA, G. U., Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Academy of Sciences, USSR

"Reaction of Trimethylsilylphosphite With 0,0-Diethylacetylphosphonate"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, p 680

Abstract: Reaction of trimethylsilylphosphite with 0,0-diethylacetylphosphonate in ether and argon atmosphere occurs with an exothermic effect yielding bis(diethylphosphone)methyltrimethylsilyloxymethane, b.p. 100°/0.003 mm, n_D^{20} 1.4430, d_4^{20} 1.1023. The structure was confirmed by NMR^{31p} and PMR spectroscopy.

USSR

UDC 547.26'118

PUDOVIK, M. A., TERENT'YEVA, S. A., MEDVEDEVA, M. D., and PUDOVIK, A. N.,
Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Academy
of Sciences, USSR

"N-Acetylated Oxazaphospholanes and Phosphorinanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, p 679

Abstract: Heating equimolar quantities of N-acylated aminoalcohols or N-acetyl-o-aminophenol with complete amides of phosphorous acid or with the diamides of alkylphosphorous acids yielded a series of 2-substituted 3-acetyl-1,3,2-oxazaphospholanes and phosphorinanes: 2-diethylamino-3-acetyl-4,5-benzo-1,3,2-oxazaphospholane, b.p. 114-115°/0.04 mm; 2-ethoxy homologue, b.p. 95-96°/0.08 mm; 3-isopropoxy homologue, b.p. 109-111/0.05 mm; 2-diethylamino homologue, b.p. 92-93° (0.1 mm), and 2-diethylamino-3-acetyl-1,3,2-oxazaphosphorinane, b.p. 100-102°/0.025 mm.

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USSR

UDC 547.26'118 + 543.226
PUDOVIK, A. N., KONOVALOVA, I. V., YAGFAROV, M. Sh., GOL'DFARB, E. I., and
ROMANOV, G. V.

"Decomposition of α -Hydroxyalkyl(benzyl)phosphonates"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 3, Mar 73, pp 556-559

Abstract: Thermal behavior of α -hydroxyalkylphosphonates containing alkyl and phenyl substituents at the α -carbon atom has been studied by means of differential-thermal analysis in the range 20-300°. Substituting a hydrogen atom for a methyl group at the α -carbon results in a higher temperature of the endoeffect of the beginning of breakdown, while introduction of a phenyl group lowers the thermal stability of the phosphonate. Differential thermal analysis of an equimolar mixture of O-ethylethylphosphonite and ethylpyro-racemate shows a formation of O-ethyl-O-(α -carboethoxyethyl)ethylphosphonate; lowered by its isomerization to O-ethyl-O-(α -carboethoxyethyl)ethylphosphonate in benzaldehyde and diethylphosphite from diethyl- α -hydroxybenzylphosphonate in temperature range 100-120° to be followed by decomposition. Thermography of phenyl- α -hydroxybenzylphosphinic acid at 220-250° is accompanied by a strong exothermic effect yielding a dense mass suggestive of the formation of benzylphosphine.

USSR

UDC 547.341.07(088.8)

PUDOVIK, A. N., SUDOKHOVA, T. M., and YEVSTAF'YEV, G. I.

"Addition Reactions of Phosphinous Acid to Malonic Acid Dinitrile"

Doklady Akademii Nauk SSSR, Vol 208, No 1, 1973, pp 111-113

Abstract: The earlier work of the authors has shown the ease with which addition reactions proceed between dialkyl- and diarylphosphinous acids and nitriles at the nitrile group, when the reaction is activated by electro-negative groups. The current investigation is the continuation of the earlier work dealing with the elucidation of the effect of substituents of the phosphorus atom on the overall reaction rates. This article deals with gas-liquid chromatographic investigation of the reaction kinetics of a series of phosphinous acids with malononitrile. The reaction rate was monitored by the decrease of the concentration of nitrile in the reaction mixture. The investigated reactions were found to be of second order. The increase in the length of the hydrocarbon chain leads to a higher value of the energy of activation. Sodium ethoxide has a strong catalytic effect on the described reaction rates. Solvent effects are also significant.

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USSR

UDC 547.20'18

ISHMAYEVA, E. A., CHERKASOV, R. A., OVCHINNIKOV, V. V., and PUDOVIK, A. N.,
Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Dipole Moments of Oranophosphorus Compounds. X. 1,3,2-Dioxa- and
Dithiaphospholanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 42 (104), No 12, Dec 72, pp 2642-2644

Abstract: Dipole moments of the P-S bond were calculated from experimental dipole moments of 1,3,2-dithiaphospholanes. The values determined ranged from 0.26-0.25 D. The change in the bond angle S:P-Alk by $\pm 3^\circ$ with regard to the accepted value of 115° results in a change of the dipole moment of the P-S bond by ± 0.03 D. The change of the dipole moment of the P-S bond caused by the effect of the elements surrounding the phosphorus atom indicates that interactions do take place in the system under investigation.

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USSR

UDC 547.26'118

~~PIDOVIK~~ A. N., CHERKASOV, R. A., and OVCHINNIKOV, V. V., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Some Reactions of Cyclic Dithioacids of Phosphorus"

Leningrad, Zhurnal Obshchey Khimii, Vol 42 (104), No 12, Dec 72, pp 2638-2642

Abstract: Reactions of cyclic 2,3-butyleneglycoldithiophosphoric, 1,3-butyleneglycoldithiophosphoric, neopentyldithiophosphoric, and pinacolove-dithiophosphoric acids with triethyl phosphite, benzylidenemalonic ester, methylenemalonic ester, diethyl maleate, and diethyl fumarate were investigated. The reactions follow the Arbuzov rearrangement leading to the formation of full esters of cyclic dithiophosphates. By kinetic and thermographic methods it was shown that the cyclic dithiophosphates exhibit higher activity in reactions with acrylonitrile than their acyclic analogs. On the basis of kinetic studies the σ_ϕ constants for cyclic fragments of dithioacids were determined.

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USSR

UDC 547.26'118

PUDOVIK, A. N., KONOVALOVA, I. V., KAKURINA, V. P., BURNAYEVA, L. A.,
and KOMISSAROVA, T. A.

"Reactions of Dialkylphosphorous Acid Monoisocyanates With Esters of
Benzoylformic and α , β -Diketobutyric Acids and Phenylglyoxal"

Leningrad, Zhurnal Obschey Khimii, Vol 43(105), No 2, Feb 73, pp 256-260

Abstract: Monoisocyanates of dialkylphosphorous acids react with esters of pyruvic, benzoylformic, and α , β -diketobutyric acids and phenylglyoxal in methylene chloride at -5° to 0° yielding 2-alkoxy-2-oxo-3-alkyl-5-substituted 2-phosphaoxazolidin-4-ones, dense liquids soluble in organic solvents, insoluble in water, and isocyanates of dialkylphosphoric acids in 15% yield. The reaction mechanism was studied by IR and NMR spectroscopic methods.

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USSR

UDC 547.26'118

PUDOVIK, A. N., ZIMIN, M. G., and SOBANOV, A. A., Kazan' State University
imeni V. I. Ul'yanov-Lenin

"Reactions of Dialkyl Phosphites With Ketones Activated by Electronegative
Groups"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 10, 1972, pp 2174-2180

Abstract: As a result of the reaction of dimethyl- and diethyl phosphites with 2-carbethoxycyclopentanone, 2-carboethoxycyclohexanone, diethylphosphonoacetone, desoxybenzoin, and the nitrile of alpha-phenylacetoacetic acid, in the presence of diethylamine, 1-hydroxy-2-carboethoxycyclopentyl (or hexyl)-, 1-hydroxy-2-diethylphosphonoisopropyl-, 1-hydroxy-1,2-di-phenylethyl-, and 1-hydroxy-2-cyano-2-phenylisopropylphosphonates were formed. Structures of the products were confirmed by elemental analysis and IR and NMR (Nuclear Magnetic Resonance) spectra, and various characterizing constants were determined. The presence of hydroxyl groups was also confirmed by reacting the esters with acetic anhydride or acetyl chloride; the constants of the resulting acetates were determined, and their IR and NMR spectra taken. On heating these esters in the presence of alkali metal alkoxides or without a catalyst, decomposition to their
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USSR

PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 42(104), Vyp 10, 1972, pp 2174-2180

original components and sometimes partial dehydration were observed, rather than a phosphonatephosphate rearrangement. Heating dialkyl 1-acetoxy-2-diethylphosphonoisopropyl-, and 1-acetoxy-2-carboethoxycyclopentyl(or hexyl)phosphonates in the presence of sodium carbonate yielded dialkyl 2-diethylphosphonopropenyl- and 2-carboethoxycyclopentenyl(or hexenyl)-phosphonates. It was demonstrated that on reacting alpha-hydroxyalkylphosphonates with thionyl chloride dialkyl alpha-chloroalkylphosphonates are formed, which eliminate hydrochloric acid on heating with pyridine to form vinylphosphonates.

2/2

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USSR

UDC 547.26'118

PUDOVIK, A. N., ZIMIN, M. G., SOBANOV, A. A., VINOGRADOV, L. I., and
SANTOV, Yu. Yu., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Reaction of Dialkyl Phosphites With Ethyl Acetoacetate and the
Dehydration of Esters of Alpha-hydroxyalkylphosphonic Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 10, 1972, pp 2167-2174

Abstract: As a result of the reaction of dimethyl, di-n-propyl, diisopropyl, di-n-butyl phosphites and the partial ethyl ester of phenylphosphorous acid with ethyl acetoacetate in the presence of diethylamine, dialkyl alpha-hydroxy-beta-carbethoxyisopropylphosphonates and the ethyl ester of alpha-hydroxy-beta-carbethoxyphenylisopropylphosphonic acid were formed. The IR and PMR (Proton Magnetic Resonance) spectra of the products were studied and constants recorded. The PMR spectrum of the diethyl ester showed that it had two nonequivalent hydrogen atoms at the beta carbon, said to be due to an internal hydrogen bond. The concentration dependence of the IR spectrum of this compound was reported to indicate intermolecular bonds between the phosphorus-oxygen double bond and the hydroxyl group in the solid state and concentrated solutions. This was confirmed by ebullioscopy and cryoscopy. On heating the esters with a catalytic amount.

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USSR

PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 42(104), Vyp 10, 1972, pp 2167-2174

of piperidine or sodium alkoxide they were dehydrated to dialkyl alpha-methyl-beta-carbethoxyvinylphosphonates. The capacity for this dehydration depends on the presence of a mobile methylene group. Beta-dialkylphospho-beta-butyrolactone was also formed as an impurity from more vigorous thermal action, but could be converted to the vinyl ester by heating with ethanol in the presence of sodium ethoxide. The dehydration was also carried out by heating in the presence of sodium carbonate.

2/2

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USSR

UDC 547.26'118:541.49

MURATOVA, A. A., PLEKHOV, V. P., YARKOVA, E. G., and PUDOVIK, A. N., Kazan' State University Imeni V. I. Ul'yanov-Lenin

"Deamination of N,N-Diethylamidoisopropyl Phosphite in a Stannic Chloride Complex"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 2, Feb 73, pp 436-437

Abstract: Reaction of a 1:1 mixture of N,N-diethylamidoisopropyl phosphite and stannic chloride yields a complex -- a viscous colorless product which is stable only at low temperature. At room temperature it breaks down precipitating a white solid of the composition $(C_2H_5)_2NH \cdot SnCl_2$. Evidently a redox process occurs with the elimination of the P-N bond and formation of a secondary amine.

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USSR

UDC 547.341

PUDOVIK, A. N., and KHUSAINOVA, N. G., Kazan' State University

"Cycloaddition of N-Phenylsidnone to Allenylphosphonates"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), Vyp 10, 1972, pp 2162-2166

Abstract: N-phenylsidnone (4-phenyl-1,4,5-oxadiazolid-2-one) was reacted with diethyl allenylphosphonate, gamma-methylallenylphosphonate and gamma, gamma-dimethylallenylphosphonate, and dipropyl gamma, gamma-dimethylallenylphosphonate. Eight to 10 hours at 135-140° under reflux led to 1,3 bipolar cycloaddition and subsequent decarboxylation, producing the corresponding pyrazoles. Differential thermometry of the reaction mixture showed that the allenylphosphonates did not isomerize under these conditions. The Proton Magnetic Resonance spectrum of 1-phenyl-3-diethylphosphon-4-methylpyrazole suggests that two diastereomers are formed, and indicates their relative concentrations. Using differential thermometry the dipolarophilic activity of the four allenylphosphonates was shown to decrease with increased steric hindrance.

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USSR

UDC 547.341

PUDOVIK, A. N., KHUSAINOVA, N. G., and TIMOSHINA, T. V., Kazan' State University

"Cycloaddition of Diphenyldiazomethane to Allenylphosphonates"

Leningrad, Zhurnal Obschey Khimii, Vol 42(104), Vyp 10, 1972, pp 2159-2162

Abstract: The 1,3-bipolar cycloaddition of diphenyldiazomethane to diethyl allenylphosphonate at room temperature in petroleum ether and diethyl ester, yields 3-diethylphosphono-4-methylene-5,5-diphenyl-delta²-pyrazoline as indicated by the IR and PMR (Proton Magnetic Resonance) spectra of the product. An intermediary delta¹-pyrazoline is suggested. If the reaction is conducted at 75°C the product indicated by the IR, PMR, and NMR (Nuclear Magnetic Resonance) spectra is 1-diethoxylphosphonyl-2-methyl-3-phenylindene. An intermediate of 2,2-diphenyl-3-diethoxylphosphonylmethylenecyclopropane is proposed. At both room temperature and 75°C diphenyldiazomethane reacted with diethyl alphaphenylallenylphosphonate to give 3-diethoxyphosphonyl-2,2,3-triphenylmethylenecyclopropane, as confirmed by the IR spectrum of the product. An intermediary delta¹-pyrazoline is indicated, which cannot rearrange to the delta²- as the 3 hydrogen has been replaced by a phenyl group.

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UDC 547.341 + 547.235

PUDOVIK, A. N., BATYYEVA, E. S., and YASTREMSKAYA, N. V., Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Acad. Sc. USSR

"A New Synthetic Method for Substituted 1,2-Azaphospholanes"

Leningrad, Zhurnal Obshchey Khimii, Vol 43 (105), No 2, Feb 73, pp 437-438

Abstract: O,O-Diethyl amidophosphite reacts with the N-phenylamide of acrylic acid yielding O,O-diethyl N-phenylamido- β -N-phenylcarbamoylethylphosphonate, m.p. 85°, which on distillation under high vacuum eliminates ethylaniline to form a cyclic product, 2-ethoxy-1-phenyl-2,5-dioxo-1,2-azaphospholane, b.p. 157-160°/0.007 mm n_D^{20} 1.5490, m.p. 71-73°.

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USSR

UDC 547.26'118

PUDOVIK, A. N., ZIMIN, M. G., YEVDOKIMA, V. V., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Reactions of α -Ketophosphonates with Ethyl Cyanoacetate and Malononitrile"
Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), No 7, Jul 72, pp 1489-1493

Abstract: Continuing their research on the activity of the carbonyl group in addition reactions with α -ketophosphonic acid esters, the authors studied the behavior of these phosphonates with ethyl cyanoacetate and malononitrile. Reactions of diethyl aceto- and benzoylphosphonates with ethyl cyanoacetate at 120°C in the presence of catalytic quantities of piperidine or diethylamine produced diethyl α -methyl(phenyl)- β -cyano- β -carboethoxyvinylphosphonates in 26-27% yield. The reactions are accompanied by considerable tarring and formation of large quantities of low-boiling fractions. The resultant vinylphosphonates (II) were identified by ultimate analysis and their IR spectra. Malononitrile reacted with dimethyl, diethyl, di-n-propyl and diisopropyl acetophosphonates, and with diethyl and di-n-butyl benzoylphosphonates. Addition of catalytic quantities of piperidine to the initial mixture of components causes heating to 70-100°C. The reaction products in the case of the dialkyl acetophosphonates were dialkyl α -methyl- β -car-

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PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 42(104), No 7, Jul 72,
pp 1489-1493

hamido- β -cyanovinylphosphonates (V). The reactions with benzoylphosphonates
yielded dialkyl α -phenyl- β , β -dicyanovinylphosphorates.

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USSR

UDC 547.26'118

PURCOV, A. N., SUDAKOVA, T. M., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Addition of Phosphinous Acids to the Nitrile Group"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(104), No 7, Jul 72, p 1646

Abstract: Phosphinous acids add to the triple $C\equiv N$ bond of nitriles, resulting in synthesis of oxides of substituted iminophosphines. Diphenylphosphinous acid reacted with benzonitrile in the presence of catalytic quantities of sodium alkoxide to give diphenyl(aminophenyl methyl)phosphine oxide, and phosphinous acids reacted with chloroacetonitrile with replacement of the chlorine in the chloroacetonitrile accompanied by liberation of hydrogen chloride, after which a second molecule of phosphinous acid adds to the resultant dialkyl(aryl)phosphinoacetonitrile.

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USSR

UDC 542.91:547.1'118

PUDOVIK, A. N., BATYIEVA, E.S., and NESTERENKO, V. D., Institute of Organic and Physical Chemistry Imeni A. Ye. Arbuzov, Acad. Sc. USSR

"Reaction of N-Arylamides of Dialkylphosphorous and Diarylphosphinous Acids With Benzyl"

Moscow, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 4, Apr 72, pp 871-875

Abstract: N-Arylamides of dialkylphosphorous and diarylphosphinous acids react with benzyl forming respective imidophosphites and imidophosphonates. To 4.2 g of the diethylphosphorous acid anilide in 50 ml ether, 4.2 g of benzyl in 100 ml ether was added dropwise with stirring and in an atmosphere of nitrogen. After a 30 min reaction at room temperature, the solvent was removed, the residue was evacuated down to 0.08 mm for 30 min, to yield a light yellow liquid. In an analogous manner, diethyl- δ -benzoylbenzyl-N-tolylimidophosphate was obtained from toluidide and benzyl. When diethyl- δ -benzoylbenzyl-N-phenylimidophosphate (I) was reacted with CS_2 , phenylisothiocyanate, m.p. 52-55° was obtained: with water (I) gave diethylanilidophosphate, m.p. 93°. The anilide of diphenylphosphinous acid treated with benzyl, followed by CO_2 gave diphenylanilidophosphate, m.p. 234° and δ -benzoylbenzyl-diphenylphosphinate, m.p. 128-130°.

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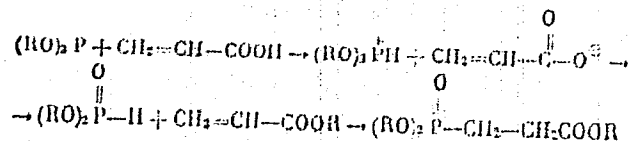
UDC 542.91:661.718.1

GAZIZOV, T. Kh., MAREYEV, Yu. M., VINOGRADOVA, V. S., PUDOVIK, A. N., and ARBUZOV, B. A., Chemistry Institute imeni A. M. Butlerov, Kazan' State University imeni V. I. Ul'yanov-Lenin, and Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Interaction of Trialkyl Phosphites with α, β -Unsaturated Acids"

Moscow, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 6, Jun 71, pp 1259-1266

Abstract: Experimental material indicates that the addition of trialkyl phosphites to α, β -unsaturated acids may proceed by preliminary protonation of the trialkyl phosphites by the unsaturated acids, with subsequent addition of the resultant dialkylphosphorous acids to esters of the unsaturated acids to give trialkyl esters of the corresponding β -phosphonocarboxylic acids, according to the scheme



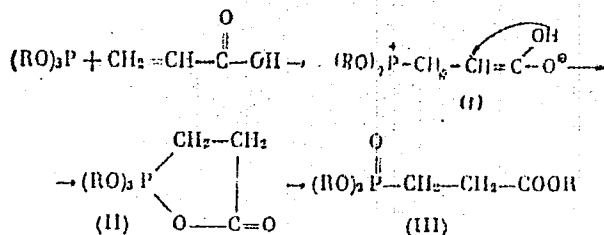
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GAZIZOV, T. Kh., *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No 6, Jun 71, pp 1259-1266

It is also possible that these reactions proceed according to the scheme suggested by V. A. KUKHTIN and G. Kh. KAMAY, viz.



but without the formation of an intermediate cyclic product of the phosphorane type. The reaction may proceed simultaneously according to both schemes.

The interaction of triethyl phosphite with acrylic acid, along with trimethyl ester of β -phosphonopropionic acid, gives a small amount of the cyclic anhydride of methyl ester of β -phosphonopropionic acid. The latter is obtained in much greater quantities in the presence of acetic acid. The

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GAZIZOV, T. Kh., et al., Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 6, Jun 71, pp 1259-1266

formation of an analogous cyclic anhydride is observed in the interaction of triethyl phosphite with methacrylic acid, as well as in the presence of acetic acid.

The authors thank E. I. GOL'DFARB for taking the NMR spectra.

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USSR

UDC 547.241+547.391.1

GAZIZOV, T. Kh., VASYANINA, M. A., PASHINKIN, A. P., ANOSHINA, N. P.,
GOL'DFARB, Z. I., and PUDOVIK, A. N., Institute of Organic and Physical
Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Mechanism of the Reaction of Diethyl Chlorophosphite With Acrylic Acid"

Leningrad, Zhurnal Obshchey Khimii, Sep 71, Vol 41, No 9, pp 1957-1961

Abstract: The study of the reaction of diethyl chlorophosphite with acrylic acid using P^{31} NMR and thermography gives rise to the conclusion that protonation of the phosphorus atom either completely initiates or predominates in the reaction which is followed by the addition of diethylphosphorus acid (an intermediate product formed in the early stage of the reaction) to the acrylic acid chloride. The experimental portion of the paper covers in detail the reactions of diethyl chlorophosphite with acrylic acid, diethyl acroyl phosphite with hydrogen chloride and diethylphosphorous acid with acrylic acid chloride.

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USSR

UDC 547.26'118

TOROPOVA, V. F., CHERKASOV, R. A., SAVEL'YEVA, N. I., GRIGOR'YEVA, L. A.,
SHERGINA, I. V., OVCHINNIKOV, V. V., and PUDCOVIK, A. N., Kazan' State
University imeni V. I. Ul'yannov-Lenin

"Study of Stability of Complexes of Silver, Nickel and Cobalt Ions With
Phosphorus Dithioacid Derivatives"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 8, Aug 71, pp 1673-1676

Abstract: A study was made of the composition and stability of complex
compounds of silver ions with a series of phosphorus dithioacid derivatives,
as well as complexes of nickel and cobalt ions with diethyldithiophosphoric
acid by the potentiometric method in a 90-percent ethanol-aqueous solution at
an ionic strength of 0.3 and a temperature of 25°. Stability constants
($\log \beta_2$) are determined and correlated with constants for substituents
at the phosphorus atom in the molecule of the ligand, particularly for the
2,3-butylene glycol substituent.

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USSR

UDC 547.26'118:541.49

YARKOVA, E. G., MUSINA, A. A., PLEKHOV, V. P., MURATOVA, A. A., and
PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Electron Effect of an Acceptor on the Rotational Isomers of Certain
 Organophosphorus Ligands"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,576-2,577

Abstract: Infrared and paramagnetic resonance spectral data on several rotational isomers of organophosphorus ligands were obtained. Specifically, the complex $[(CH_3O)C_2H_5P(O)H]_2 \cdot SnCl_4$ exhibited the presence of the 1040, 1060, and 810, 823 cm^{-1} bands, instead of the two bands ν_{C-O} (1030 and 1070 cm^{-1}) and ν_{P-O} (790 and 805 cm^{-1}) in the spectrum of the methyl ester of ethylphosphonous acid, while unexpected doublets appeared in the p. resonance spectrum of the starting ester. The existence of complexes with several different isomers of the methyl ester of ethylphosphonous acid is suggested by the spectral data. Variation in the $^3J(P-O-C-H)$ constants suggests a mesomeric effect in the case of one isomer, owing to its favorable spatial location, with corresponding reduction in length of the P-O bond and a certain loosening of the O-C bond. Other structural effects are postulated.

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USSR

UDC 541.67

ISHMAYEVA, E. A., RAYEVSKIY, O. A., CHERKASOV, R. A., KHALITOV, V. V., and
PUDOVIK, A. N., Kazan' State University imeni V. I. Ulyanov-Lenin, Institute
of Organic and Physical Chemistry imeni A. Ye. Arbuzov, USSR Academy of
Sciences, Kazan'

"Estimating the Dipole Moment of the P-S Bond"

Moscow, Doklady Akademii Nauk SSSR, 1971, Vol 197, No 4, pp 862-864

Abstract: Successful use of the dipole-moment method in structural studies depends largely upon a rational choice of the moments of the individual bonds. In addition, special difficulties arise in connection with calculating the dipole moments of ordinary bonds in which rotation is possible. There is no published information on the dipole moment of the P-S bond, which, apart from being of interest in itself, would make possible extension of use of the dipole-moment method to the structure of organophosphorus compounds.

The authors studied experimentally the dipole moment of 2-thiono-2-methyl-1,3,2-dithiaphosphorine, and applied infrared spectroscopy to determine the dipole moment of the P-S bond.

It was found that the negative end of an ordinary P-S bond is the phosphorus, just as it is in the case of the P-O bond. Various graphic data on the infrared spectra of the above-noted compounds accompany the paper.

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USSR

UDC 547.26'118

PUDOVIK, A. N., PUDOVIK, M. A., TERENT'YEVA, S. A., and BEL'SKIY, V. Ye.,
Kazan' Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov,
USSR Academy of Sciences

"Reaction of 1,3,2-Oxaazaphospholanes With Alcohols and Mercaptans"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,407-2,413

Abstract: This is a continuation of an earlier study in which the authors demonstrated that 1,3,2-oxaazaphospholanes with a dialkylamino group at the phosphorus atom are readily subject to alcoholysis, with formation of the corresponding alkoxy derivatives; here the reaction of certain derivatives of the 1,3,2-oxaazaphospholanes with alcohols and mercaptans is studied. Derivatives tested were 2-ethoxy-4-methyl-N-methyl-1,3,2-oxaazaphospholane, 2-ethoxy-N-phenyl-1,3,2-oxaazaphospholane, 2-propoxy-1,3,2-oxaazaphospholanes, 2-chloro-N-phenyl-1,3,2-oxaazaphospholane, and 2-diethylamino-N-phenyl-1,3,2-oxaazaphospholane; reactants were ethyl and propyl alcohols, phenylaminoethanol, aliphatic mercaptans, propyl mercaptan and thiophenol. It was found that replacement of the alkyl group at the nitrogen atom of the phospholane ring with a phenyl group leads to definite stabilization of the

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PUDOVIK, A. N., et al., Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,407-2,413

ring; further, the above-indicated reactions with aliphatic mercaptans proceed with elimination of sulfur from the mercaptans and formation of the corresponding thion derivatives. The reaction with thiophenol produces thiophosphite; that with benzylmercaptan, both thiophosphite and dithiophosphate.

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USSR

UDC 547.26'118

GAZIZOV, T. Kh., PASHINKIN, A. P., and PUDOVIK, A. N.

"Reaction of Tetraethyl Pyrophosphite With the Halogens, Acetyl Chloride, and Acrylic Acid"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,418-2,420

Abstract: The published information on the reactivity of tetraalkyl pyrophosphites toward various electrophilic reagents is limited; here the reactions of tetraethylpyrophosphite with chlorine, bromine, acetyl chloride and acrylic acid are studied. In the reaction with the first three reagents, the corresponding acyl halides were formed in addition to diethyl halophosphates and diethyl acetophosphonate. In the case of the reaction with acrylic acid, diethylphosphorous acid was formed, along with diethyl acryloylphosphite.

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USSR

UDC 547.26'118

PUDOVIK, A. N., KONOVALOVA, I. V., and BURNAYEVA, Kazan' State University
imeni V. I. Ul'yanov-Lenin

"Reactions of Phosphite Esters With Phenylglyoxal and the Ethyl Ester of α , β -Diketobutyric Acid"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,413-2,417

Abstract: This study is a continuation of earlier work on the reactions of tri- and pentavalent phosphorus acids with carbonyl compounds; here the reactions of dialkylphosphorous acids with phenylglyoxal and the ethyl ester of α , β -diketobutyric acid are studied. It was shown that the dialkylphosphorous acids add to phenylglyoxal and to the ethyl ester of α , β -diketobutyric acid, with formation of benzoyl- and acetocarbethoxyhydroxymethyl-dialkylphosphonates. The latter, on heating, were isomerized into benzoyl- and acetocarbethoxymethyldialkylphosphates. In the reaction of phenylglyoxal and the ethyl ester of α , β -diketobutyric acid with triethyl phosphite in acetic acid, the same phosphates were formed. Finally, the reaction between phenylglyoxal and the ethyl ester of α , β -diketobutyric acid, with phosphites in a solution of methylene chloride produced 1,3,2-dioxaphospholenes.

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USSR

UDC 547.341

PUDOVIK, A. N., KHUSAINOVA, N. G., and FROLOVA, T. I.

"1,3-Bipolar Addition of N-Phenylsydnone to Esters of Propynylphosphonic and Propynylthiophosphonic Acids and to Diphenylpropynylphosphine Oxide"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 11, Nov 1971, pp 2,420-2,424

Abstract: 1,3-Bipolar addition to phosphorus-containing acetylenes is not well known. Cycloaddition was achieved by running the indicated reactions at 130-150° for 10-12 hrs. N-Substituted phosphonpyrazoles were obtained in yields of 65-80%. 1-Phenyl-3-diphenylphosphin oxide-4-methylpyrazole and four different 1-phenyl-3-dialkyloxy(thio)phosphono-4-methylpyrazoles were obtained. Yields, formulas, physical constants, etc., for these are given.

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USSR

UDC 547.558.1

KONOVALOVA, I. V., and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

"Reactions of Trivalent Phosphorus Acid Derivatives With Carbonyl Containing Compounds"

Moscow, Uspekhi Khimii, Vol 41, No 5, May 72, pp 799-827

Abstract: A review with 188 references covering the reactions of neutral esters of phosphorous acid, amidophosphites, and mixed anhydrides of dialkylphosphorous and carboxylic acids with carbonyl compounds containing no halogen atoms: saturated and unsaturated aldehydes and ketones, α -diketones, carbonyl compounds activated by a carbethoxy, a phosphoryl, a nitrile or some other electronegative group. The directions of these diverse and very interesting reactions and their mechanisms have been analyzed in light of their importance in the development of the chemistry of phosphorus compounds and theoretical organic chemistry.

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USSR

UDC 547.26'118

PUDOVIK, A. N., KONOVALOVA, I. V., ROMANOV, G. V., and NAZMUTDINOV, R. Ya.,
Kazan State University

"Reaction of Partial Esters of Phenylphosphonous and Phosphorous Acids With
Benzophenone"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(103), No 2, Feb 72, pp 323-326

Abstract: O-Methyl- and O-ethyl phenylphosphonites, and also dimethyl-, diethyl-, di-n.-propyl- and di-isopropyl phosphites reacted with benzophenone. It was found that the partial esters of phenylphosphonous and phosphorous acids add to benzophenone with the formation of monoalkyl esters of α -hydroxybenzhydrylphenylphosphinic and dialkyl esters of α -hydroxybenzhydrylphosphonic acids. When heated, α -hydroxybenzhydrylphosphinates and phosphonates dissociate into the initial products and undergo rearrangement to the corresponding phosphonates and phosphates.

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USSR

UDC 547.26'118

PIIDOVIK, A. N., KONOVALOVA, I. V., and KAKURINA, V. P., Kazan' State
University imeni V. I. Ul'yanov-Lenin

"Reactions of Dialkyl Anilidophosphites with α -Ketocarboxylic Acid Esters"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(103), No 2, Feb 72, pp 333-337

Abstract: The authors investigate reactions of ethyl benzoylformate with anilido- and p-toluidinodiethylphosphites. It is shown that these reactions result in formation of 0,0'-diethyl-0''- α -carboethoxybenzyl-N-phenylimido-phosphates. It is found that 0,0'-diethyl 0''- α -carboethoxyethyl N-phenylimidophosphate reacts with the second molecule of the pyruvic ester to form diethyl α -carboethoxyethyl phosphate. Reactions of diphenyl anilidophosphinite with pyruvic, benzoylformic and mesoxalic acid esters take place with the formation of diphenylanilidophosphine.

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USSR

UDC 547.26'118

PUDOVIK, A. N., MURATOVA, A. A., KURAMSHIN, I. Ya., and YARKOVA, E. G.,
Kazan' State University imeni V. I. Lenin-Ul'yanov

"IR-Spectral Study of the Reaction of Some Methylphosphonic Acid Chlorides
With Tin Tetrachloride"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(103), No 2, Feb 72, pp 317-322

Abstract: The authors investigated the reaction of stannic tetrachloride with methylmonothiophosphonic acid dichloride and with the acid chlorides of O,O'-dimethylmonothiophosphoric, O-methylmethyl-, O-n.-butylmethyl-, O-isobutylmethyl-, and O-sec.-butylmethylmonothiophosphonic acids. It is found that the donor capacity of the phosphoryl oxygen with respect to stannic chloride is greater than that of the thiophosphoryl group which increases with a reduction in the $\Sigma\sigma_p$ of the substituents at the phosphorus atom. It is shown that when O-alkylmethylmonothiophosphonic acid chlorides react with stannic chloride, formation of an unstable intermediate complex via the phosphoryl group takes place on the first stage, while thion-thiol isomerization and dealkylation takes place at the second step of the reaction.

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USSR

UDC 547.26'118:541.49

PUDOVIK, A. N., MURATOVA, A. A., MEDVEDEVA, M. D., YARKOVA, E. T., and
LOGINOVA, E. I., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Investigation of the Reaction of Diethylphosphinous Acid Esters With
Trialkyl and Dialkyl Halides of Tin"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(103), No 2, Feb 72, pp 327-333

Abstract: The authors study reactions of methyl, ethyl, n -propyl, isopropyl, n-butyl and n -hexyl esters of diethylphosphinous acid with triethyl and diethyl chlorides, bromides and iodides of tin. It was found that diethylphosphinous acid esters react with trialkyl and dialkyl halides of tin to form stable complexes containing trialkylphosphine oxide and an alkyl halide of tin. As the radical of the alkoxy group increases, the reactivity of the phosphinite in these reactions decreases. The activity of alkyl halides of tin drops with a transition from dialkyl to trialkyl halides, and also with a transition from iodine to chlorine derivatives of tin.

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USSR

UDC 547.26'118:541.4

PUDOVIK, A. N., MURATOVA, A. A., and MEDVEDEVA, M. D., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Reaction of Phosphinites With Titanium Tetrachloride"

Leningrad, Zhurnal Obshchey Khimii, Vol 42(103), No 2, Feb 72, p 469

Abstract: It was shown that O-alkyl diethyl- and O-alkyl di-phenyl-phosphinites react with titanium tetrachloride at -40 to -50°C to form extremely unstable intermediate crystalline complexes $(\text{R}_2\text{POR}')\cdot\text{TiCl}_4$. The structure of the resultant compounds is confirmed by IR-spectroscopy. Intermediate complexes $[(\text{C}_2\text{H}_5)_2\text{POR}]\cdot\text{TiCl}_4$ eliminate alkyl halide to form a viscous dark green product -- interstitial complex $(\text{C}_2\text{H}_5)_2\text{P}\cdot\text{OTiCl}_3$. Intermediate compound $[(\text{C}_6\text{H}_5)_2\text{POC}_2\text{H}_5]\cdot\text{TiCl}_4$ is analogously converted to $(\text{C}_6\text{H}_5)_2\text{P}\cdot\text{OTiCl}_3$.

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USSR

UDC 547.341

PUDOVIK, A. N., YASTREBOVA, G. YE., CHERKOSOVA, O. A.

"The Reactions of Condensation and Addition of the Diethyl Ether of Carbamoylphosphonic Acid"

Leningrad, Zhurnal Obshchey Khimii, Vol XLII (CIV), No 1, 1972, pp 88-90

Abstract: It has been demonstrated [A. N. Pudovik, et al., DAN SSSR, No 90, 799, 1953; A. N. Pudovik, et al., ZhOKh, No 36, 1232, 1966] that organophosphorus compounds with an active methylene radical -- the diethyl esters of cyanomethyl, acetomethyl and carboethoxymethylphosphonic acids -- easily enter into the reaction of condensation with aldehydes under the conditions of basic catalysis. As a continuation of this research, a study was made of analogous reactions with the diethyl esters of carbamoylmethylphosphonic and carbalkoxymethylphosphonic acids. As a result of condensations of diethyl ether of carbamoylmethylphosphonic acid with benzoic, cinnamic aldehydes, para-substituted benzaldehydes and furfural, the diethyl esters of α -carbamoyl- β -phenylvinylphosphonic acids were obtained. The addition of diethyl ether of carbamoylmethylphosphonic acids to the nitrile of acrylic acid and methyl ester of acrylic acid was realized. The reaction took place in the presence of sodium ethylate. They are accompanied by a significant exothermic effect and lead to the formation of the addition products with yields of 40-53%.

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USSR

UDC 547.26'118

PUDOVIK, A. N., CHERKASOV, R. A., BYKOVA, I. V., YEVSTAF'YEV, G. I., ZEMSKAYA, Z. I., NAZYP'OV, M. N.

"Interaction of Tetraalkyl(aryl)stannates with Phosphorus Dithio Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol XLII (CIV), No 1, 1972, pp 76-80

Abstract: The interaction of tetraethyl lead with dithio acids of phosphorus taking place with breaking of one, two or three Pb-C bonds and the formation of the corresponding organolead dithiophosphates has been described [A. N. Pudovik, ZhOKh, No 41, 1472, 1971]. As a continuation of this research, a study was made of the reaction of phosphorus dithio acids with the tetraalkyl derivatives of tin. The dealkylation of the tetraalkyl(aryl)stannates of phosphorus dithio acids takes place with breaking of the Sn-C bond and lead to the formation of trialkyl(aryl)stannyl derivatives of dithiophosphates and phosphonates. The methods of gas adsorption chromatography and differential-thermal analysis were used to study the relative reactivity of tetraalkyl(aryl)stannates. The ease of stripping off the radicals connected to the tin atom decreases in the following series C_6H_5 , C_2H_5 , C_3H_7 , C_4H_9 . Preliminary data are presented on the fungicidal and fungistatic activity of organotin dithiophosphates and phosphonates, their anthelmintic and insecticidal activities. High activities in all these areas were generally demonstrated.

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UDC 547.512+547.341+547.722.2

PUDOVIK, A. N., CAREYEV, R. D., STABROVSKAYA, L. A., YEVSTAF'YEV, G. I.,
REMLZOV, A. B.

"Cyclic Addition of Diazoalkanes to Isopropenylphosphonates"

Leningrad, Zhurnal Obshchey Khimii, Vol XLII (CIV), No 1, 1972, pp 80-87

Abstract: A study was made of the reactions of diazomethane with esters of isopropenylphosphonic acid. By the addition of diazomethane to isopropenylphosphonates, the corresponding phosphorylated Δ^1 -pyrazolines were obtained which quickly isomerized into Δ^2 -pyrazolines in the presence of bases. By ultraviolet spectroscopy it was established that the tetrahedral phosphorus atom interacts by its d-orbitals with the π -orbital of the C=N radical. With respect to capacity to enter into conjugation it is inferior to the ester carbonyl radical. The concentration and temperature infrared spectroscopy showed that the 3 and 5-phosphorylated Δ^2 -pyrazolines are associated at the expense of the intermolecular hydrogen bonds.

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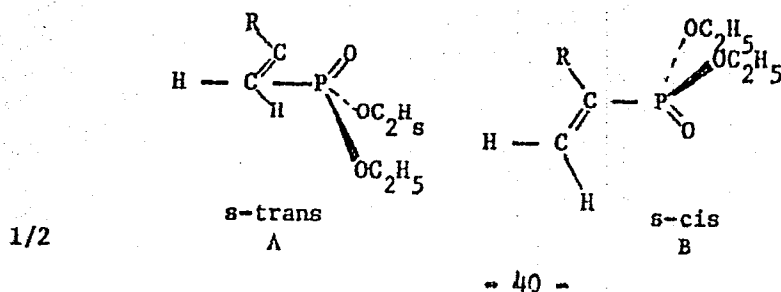
UDC 547.341

ISHMAYEVA, E. A., GAREYEV, R. D., YASTREBOVA, G. YE. ~~PUDOVIK, A. N.~~

"Dipole Moments of Organophosphorus Compounds. IX. Vinylphosphonate and vinylphosphin oxides"

Leningrad, Zhurnal Obshchey Khimii, Vol XLII (CIV), No 1, 1972, pp 73-76

Abstract: As a continuation of studies of organophosphorus compounds [E. A. Ishmayeva, et al., *Izv. AN SSSR, ser. khim.*, 2695, 1970] by the method of dipole moments to establish their spatial structure and electron density distribution, the dipole moments of the diethyl esters of α -methyl, α -cyano and α -bromovinylphosphonic acids were determined. The possible conformers of these compounds are represented as follows:



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ISHMAYEVA, E. A., et al., Zhurnal Obshchey Khimii, Vol XLII (CIV), No 1, 1972, pp 73-76

The ratio of the s-cis and s-trans-conformers in the α -substituted vinylphosphonates and their relative stability were determined by the electrostatic interaction of the dipoles. The presence of the rotational isomerism with respect to the C_{sp^2} -P bond was established in the diethyl ester and the acid dichloride of β -butoxyvinylphosphonic acid. The effective dipole moments of the C_{sp^2} -bonds in the oxides of vinylphosphines indicate conjugation of the vinyl and $P(O)R_2$ radicals.

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USSR

UDC 539.143.43:661.718.1

ISHMAYEVA, E. A., BONDARENKO, N. A., and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

"Dipole Moments of Para-Substituted Styryl Phosphonates"

Moscow, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 11, Nov 71, pp 2565-2567

Abstract: Using the addition reaction of PCl_5 to para-substituted styrenes, the authors synthesized the acid dichloride and diethyl ester of p-chlorostyrylphosphonic acid, determined their dipole moments and calculated the moment of the interaction of chlorine in the para position of the phenyl ring with the diethoxyphosphono group (1.12 D). This value indicates that the diethoxyphosphono group plays an important part in the general conjugation chain. The authors also determined the dipole moment of styrylphosphonic acid dichloride (3.14 D). The diethoxyphosphonic group and phenyl ring in the diethyl esters of p-halogen- and p-nitro- α -cyanostyrylphosphonic acids are in the transposition.

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USSR

UDC 547.26.118

PUDOVIK, A. N., PUDOVIK, M. A., TERENT'YEVA, S. A., Institute of Organic and Physical Chemistry imeni A. YE. Arbuzov, Academy of Sciences USSR

"Reaction of 1,3,2,-Oxazaphospholanes With Glycols"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 10, 1971, pp 2177-2180

Abstract: In a continuing study of the five-membered phosphorus heterocycles, the reactions of 2-diethylamino-N-phenyl-1,3,2-oxazaphospholane (I) have been investigated with glycol, 1,2- and 1,3-propanediols. The product of the reaction with glycol was identified as 2- β -(phenylamino)ethoxy-1,3,2-dioxaphospholane (II) on the basis of NMR and IR spectra and the elemental analysis data. The structure of (II) was confirmed by identity of its NMR and IR spectra with those of the reaction product of 2-diethylamino-1,3,2-dioxaphospholane with phenylaminoethanol and by the IR spectrum of the acetylation product of (II). The mechanism of (I) reaction with glycol may involve formation of an

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PUDOVIK, A. N., et al, Zhurnal Obshchey Khimii, Vol 41, No 10, 1971, pp 2177-2180

intermediate 2- β -(hydroxyethoxy)-N-phenyl-1,3,2-oxazaphospholane which then rearranges to a spiran derivative which in turn changes to (II). The spiran derivative was detected in the reaction product of 2-chloro-N-phenyl-1,3,2-oxazaphospholane with glycol in solution at a low temperature and in the presence of triethylamine and also in (II) after one month's storage. The final products of the (I) reactions with 1,2- and 1,3-propanediol were 2-(β -(phenylamino)ethoxy)-4-methyl-1,3,2-dioxaphospholane and 2-(β -(phenylamino)ethoxy)-1,3,2-dioxaphosphorinane, respectively. The experimental procedures are described and IR spectra of (II) are shown.

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USSR

UDC 547.26.118

PUDOVIK, A. N., PUDOVIK, M. A., IVANOVA, L. K., Institute of Organic and Physical Chemistry imeni A. YE. Arbuzov, Academy of Sciences USSR

"Reaction of 1,3,2-Oxazaphospholanes With Chloral"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 10, 1971, pp 2180-2184

Abstract: The study of the interaction between 1,3,2-oxazaphospholanes with different substituents at the P atom and chloral was prompted by the previously reported discovery of strong insecticidal activity of some phosphates prepared by the reaction of dioxaphospholanes with chloral. All reactions were conducted in an ether solution with cooling. The reactions of chloral with 2-diethylamino-N-phenyl-, 2-phenoxy-N-methyl-, 2-ethoxy- or 2-propoxy-N-methyl-, or N-phenyl-1,3,2-oxazaphospholanes, all with only one ester bond in the ring, led, via ring opening, to the formation of, respectively, β , β -dichlorovinyl N,N-diethyl-N',N'-(β -chloroethyl)phenylphosphorodiamidate (I), phenyl, ethyl, or 1/2

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PUDOVIK, A. N., et al, Zhurnal Obshchey Khimii, Vol 41, No 10, 1971, pp 2180-2184

propyl β, β -dichlorovinyl N,N-(β -chloroethyl)methylamidophosphates (II, III, IV), and ethyl or propyl β, β -dichlorovinyl N,N-(β -chloroethyl)phenylamidophosphates (V, VI). In contrast to 1, 3, 2-oxazaphospholanes, the reaction of 2-propoxy-N,N'-di(sec-butyl)-1,3,2-diazaphospholane with chloral proceeds without ring opening. In contrast to dioxaphosphorinanes, 2-alkoxy-1,3,2-oxazaphosphorinanes give with chloral open-chain products, e.g., β, β -dichlorovinyl N-(γ -chloropropyl)amidophosphate with a strong intermolecular hydrogen bond. The structure of the cited reaction products was determined by IR and NMR spectra. The spectra of (III) are given, physical constants and formulas of I-VI compounds are tabulated, and preparation procedures are described. The II-VI compounds exhibited a good fungicidal activity at a sufficiently high toxicity.

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USSR

UDC 542.91:661.718.1

YELISEYENKOV, V. N., BUREVA, N. V., and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Academy of Sciences USSR

"Reaction of Amidophosphites With Dialkylphosphoric and Dialkylthiophosphoric Acids"

Moscow, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya , No 9, Sep 71, pp 2013-2018

Abstract: The authors studied reactions of amidophosphites and phosphorous acid amides with dialkylphosphoric and dialkylthiophosphoric acids. It was found that these reactions result in the elimination of amine and the formation of ester-amides of subphosphoric or subthiophosphoric acid. The reaction is reversible. The resultant anhydrides react with sulfur with evolution of heat to give ester-amides of mono- and dithiopyrophosphoric acid. The authors found a simple and convenient method for the synthesis of these ester-amides in one step without elimination of the intermediate anhydrides.

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USSR

UDC 547.26'118

MURATOVA, A. A., YARKOVA, E. G., KURAMSHIN, I. YA., and PUDOVIK, A. N.,
Kazan' State University imeni V. I. Ul'yanov-Lenin

"Study of the Reaction of Phosphorus Monothioacids With Tin Tetrahalides"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 8, Aug 71, pp 1668-1672

Abstract: For purposes of establishing the coordination center in monothio-phosphoric acid esters during their reaction with tin tetrahalides, the authors studied the IR spectra of complexes of O,O-diethyl-, O,O-di-butyl-monothio phosphates and O-methyl methylmonothio phosphonate with stannic chloride and bromide, as well as the complex of O,O,S-triethyl thiophosphate with stannic chloride. It was found that complexing is due to donor properties of the oxygen of the phosphoryl group. The absorption bands of complexes of the acids with stannic chloride and bromide at 2470-2500 cm^{-1} and solutions in chloroform and carbon tetrachloride at $\sim 2570 \text{ cm}^{-1}$ and solutions in benzene at $\sim 2520 \text{ cm}^{-1}$ are assigned to stretching vibrations of the sulfhydryl group.

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USSR

UDC 547.341

PUDOVIK, A. N., GAREYEV, R. D., AGANOV, A. V., and STABROVSKAYA, L. A.,
Kazan State University imeni V. I. Ul'yanov-Lenin

"The Reaction of Dimethoxyisopropenyl Phosphonate with 2-Diazopropane"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 5, May 1971, p 1173

Abstract: 3-Methyl-3-dimethoxyphosphinyl-5,5-dimethyl- Δ' -pyrazoline (I) is formed at room temperature by the reaction of the dimethyl ester of isopropenylphosphonic acid with 2-diazopropane, with a yield of 73.4%. No isomerization of Δ' -pyrazoline takes place. Compound I is easily converted to 3-diphenoxyphosphinyl-3-methyl-5,5-diphenyl- Δ' -pyrazoline, although, the geminal phenyl radicals are unstable at temperatures higher than 50°.

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UDC 547.26'118

YAKOVA, Ye. G., DURANSHIN, I. Ya., MURATOVA, A. A., and PUDOVIK, A. N.,
Kazan State University imeni V. I. Ul'yanov-Lenin

"Infrared Spectral Study of the Reaction of Dialkylphosphoric Acids with Tin
Tetrahalides"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 5, May 1971, pp 1003-1008

Abstract: In examining the IR spectra of dimethyl- and diethylphosphonate
complexes as formed with chlorinated and brominated tin, it was established
that the reaction occurs at the position of the oxygen in the phosphoryl group.
The structures were confirmed by spectrum analysis. It was also shown, that
in this reaction chelated compounds are formed with the liberation of hydro-
chloric acid.

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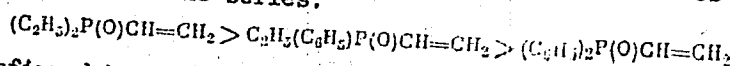
UDC 547.341+547.772.2

PUDOVIK, A. N., GAREYEV, R. D., AGANOV, A. V., RAYEVSKAYA, O. E., and
STABROVSKAYA, L. A., Kazan State University

"The Reaction of Diphenyldiazomethane with Tertiary Vinyl- and Allylphosphine
Oxides"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 5, May 1971, pp 1003-1016

Abstract: The thermal reaction (75°-80°) of diphenyldiazomethane with tertiary
phenylphosphine oxides proceeds with the formation of the corresponding Δ' -
pyrazoline intermediates. The further reaction sequence, either reduces the
pyrazolines to the related cyclopropane derivatives liberating nitrogen, or
forms the isomeric Δ^2 -pyrazolines. The comparative reactivity of oxides with
diphenyldiazomethane decreases in the series:



All structures were confirmed by IR, UV and NMR spectroscopy.

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UDC 547.341+547.772.2

PUDOVIK, A. N., GAREYEV, R. D., and AGANOV, A. V., Kazan State University

"1,3-Bipolar Addition of Diazomethane to Esters of Unsaturated Phosphonic Acids"

Leningrad, Zhurnal Obshchey Khimii, Vol 41, No 5, May 1971, pp 1017-1022

Abstract: 1,3-Bipolar addition of diazomethane to esters of vinyl-, propenyl- and allylphosphonic acids yields the corresponding Δ^2 -pyrazolines. The prototrophic isomerism which converts Δ^1 -pyrazolines to the Δ^2 form is spontaneous in this reaction sequence. The condensed form of the Δ^2 isomer forms associates at the intermolecular hydrogen bonds. All structures were confirmed by IR and NMR spectroscopy; this data and physical data on the specific compounds prepared in this work are presented.

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UDC 547.26'118:541.49

PUDOVIK, A. N., MURATOVA, A. A., MEDVEDEVA, M. D., and YARKOVA, E. G., Kazan'
State University imeni V. I. Ul'yanov-Lenin

"Study of the Reactions of Phosphonite and Phosphinite Esters With Tin
Tetrachloride"

Leningrad, Zhurnal Obshchey Khimii, Vol 41 (103), No 4, Apr 71, pp 766-771

Abstract: The reactions of trivalent-phosphorus-acid esters with SnCl_4 were carried out at a molar ratio of 2:1 in pentane or benzene at 0 to -15° under CO . When the precooled starting materials were combined, an exothermic reaction took place leading to the formation of crystalline products in most cases. It was determined that the reactions of ethyl-, phenylphosphonic, ethylphenyl-, and diphenylphosphinic acids with SnCl_4 occur in three stages: formation of the complexes $[\text{RR}'(\text{R}''\text{O})\text{P}]_2 \cdot \text{SnCl}_4$, followed by their isomerization to $[\text{RR}'\text{R}''\text{P:O}]_2 \cdot \text{SnCl}_4$, and in case of phosphonic acid complexes, elimination of alkyl halides with the formation of a P-O-Sn compound. The ease with which the first step occurs decreases in order of substituents: ethyl-, phenylphosphonic, phosphorous, ethylphenyl-, and diphenylphosphinic acid. The products are donor-acceptor type complexes in which the coordinate bond is formed by the phosphorus atom's unshared pair of electrons.

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UDC 547.26'118

PUDOVIK, A. N., GUR'YANOVA, I. V., BURNAYEVA, I. A., and KARIMULLINA, E. Kh.

"Reaction of Glycolophosphate Esters and Glycolophosphoramides With α -Ketocarboxylate Esters"

Leningrad, Zhurnal Obshchey Khimii, Sep 7i, Vol 41, No 9, pp 1978-1980

Abstract: It is shown that pyruvate esters and glyoxylates treated with glycolophosphorates and glycolophosphamides form spiro-1,3,2-dioxaphospholanes. The relatively low yield of the new product (50-65%) is attributed to the formation of oxidation products, i.e. cyclic phosphates. Spiro-1,3,2-dioxaphospholanes are dense liquids which are soluble in organic solvents. Yields, boiling and melting points and formulas of the new compounds are given.

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USSR

UDC 547.26'118

MURATOVA, A. A., KURAMSHIN, I. Ya., YARKOVA, E. G., and PUDOVIK, A. N.,
Kazan' State University imeni V. I. Ul'yanov-Lenin

"Reaction of Some Dithiophosphorus Acids With Tin Tetrahalides"

Leningrad, Zhurnal Obshchey Khimii, Sep 71, Vol 41, No 9, pp 1967-1972

Abstract: A study is presented of the reaction of 0,0-dialkyldithiophosphoric ($\text{Alk}=\text{CH}_3$, C_2H_5 , $\text{iso-C}_4\text{H}_9$) and 0-methylmethyldithiophosphonic acids with tin chloride and bromide in 2:1 and 1:1 ratios. The reaction results in the formation of products of the composition $\text{R(R')} \text{P(S)SSnX}_3$. The reaction of 0,0-dimethyldithiophosphoric acid with tin bromide results in thione-thiol isomerization concurrent with elimination of hydrogen bromide. It is shown that the donor capacity of thiophosphoryl sulfur of $\text{R(R')} \text{P(S)S-}$ to trichloro- and tribromotin salts increases with an increase in the total +I effect of the substituents at the phosphorus atom. The dissolution of the 0,0-dimethyldithiophosphoric acid -- tin bromide system in chloroform is attended by a considerable drop in the absorption intensity at 1150 cm^{-1} and an increase of absorption in the $3000\text{-}3600 \text{ cm}^{-1}$ region which points to dissociation of the isomerized complex. These spectral changes suggest that the free 0,S-dimethyldithiophosphoric acid in chloroform is primarily of a thion form, which correlates well with literature data.

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